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EARLY AGE POROSITY AND PORE SIZE DISTRIBUTION OF CEMENT PASTE WITH FLUE GAS DESULPHURISATION (FGD) WASTE

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Abstract. This paper is part of a wide-ranging investigation on the use of flue gas desulphurisation (FGD) waste in cement-based materials. It reports the results on the porosity and pore size distribution of cement paste containing varying amounts of simulated FGD waste. The water to binder ratio was 0.5. The binder consists of cement and simulated FGD. The FGD is a combination of fly ash and gypsum ranging from 0% to 100%. Cement in the pastes was partially replaced with 25% FGD (by weight). The porosity and pore size distribution of cement pastes was determined during the early stage of hydration. Increasing the amount of gypsum does not increase the pore volume. However, increasing the amount of gypsum in the paste leads to an increase in the threshold diameter and a decrease in the percentage of small pores in the paste, both indicating a coarser pore structure. The results of this investigation were compared with data at longer curing periods.

Keywords: clean coal technology; desulphurised waste; environment; flue gas desulphurisation (FGD) waste; porosity; pore size distribution; waste.

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Introduction

The coal power industry generates a substantial amount of waste worldwide. Large amounts of harmful gases such as CO_2, SO_x and NO_x are emitted into the atmosphere, thus causing environmental problems. Recently many countries in the world have adopted clean coal technology to reduce the impact of coal-fired power stations on the environment. This technology involves the use of an alkali sorbent such as lime, which can react with the SO_x gases to produce solid residues and thus preventing these gases to be emitted into the atmosphere. The solid residues are referred to as flue gas desulphurisation (FGD) waste. Depending upon the desulphurisation process, the FDG waste can range from pure gypsum to a combination of fly ash and gypsum (Mangat *et al.* 2006; Khatib *et al.* 2008). The European thermal power plants utilise brown and black coal resulting in a wide range of compositions of FGD waste. Typical FGD wastes from these plants give SiO_2 contents in the range of 28.9–65.86%, Al_2O_3 in the range of 10.71–31.9%, CaO total in the range of 1.29–47.8% and SO_3 in the range of 0.37–55.3% (Mangat *et al.* 2006). An optimum FGD composition based on strength and durability was found to be 85% fly ash and 15% gypsum providing a cement replacement of 25% (Mangat *et al.* 2006). This optimum FGD composition represents an SO_3 content of 8.87%. It corresponds to siliceous and pozzolanic active fly ashes of SO_3 content under 10% obtained from dry and semi-dry flue gas cleaning processes at many power plants in Europe. Examples of such FGD materials produced by power plants in Poland, Czech Republic, Slovak Republic and the Netherlands are given by Mangat *et al.* (2006). Pure gypsum can be used in the production of plaster board, whereas the majority of FGD consisting of gypsum and fly ash end up in landfill. This is not desirable as it raises concerns regarding the limited space of landfill sites and the impact on the environment.

Cement-based mortars and concrete are potential materials where the FGD waste can be incorporated.

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Introducing FGD waste material into concrete will affect its properties and performance. These include porosity and pore size distribution. Porosity is a measure of accessible voids with respect to the total volume of the solid material. In addition to the volume of pores, it is also important to measure the pore structure according to pore diameter, extent and shape of the pores, all of which inevitably determine the performance and utilisation of materials. The strength and durability properties of materials such as concrete depend heavily on the amount of pores present as well as the size and distribution of such pores. The influence of porosity and pore size distribution on the physical, mechanical and durability properties is well documented (Odler, Rößler 1985; Fukaya *et al.* 1991; Mangat, Khatib 1992; Calleja 1986). Many attempts have been made to correlate porosity and pore structure with the performance of paste, mortar and concrete (Nyame, Illston 1980; Kolias 1994). The findings tend to indicate that strength is related to total porosity, whereas durability tends to be influenced more by pore structure.

The effects of fly ash and other mineral admixtures on porosity and pore structure of blended cement paste, with for example fly ash or slag, is well documented in the literature (Wee *et al.* 1995; Khatib, Mangat 1995; Singh, Garg 1996; Siddique, Khatib 2010; Hadjsadok *et al.* 2012). However, there is little information in the literature on the use of FGD residues in cement-based materials. If FGD wastes residues are to be used in construction materials such as concrete, the basic properties of concrete containing these wastes need to be determined. Among these properties are the porosity and pore size distribution. This paper is part of a wider investigation on the use of FGD wastes in concrete applications. It reports the results on porosity and pore size distribution of pastes containing simulated FGD at the age of 1 day of curing (i.e. during the early age of hydration). The results at longer curing ages are reported elsewhere (Khatib *et al.* 2013a, b). Simulated FGD was a combination of fly ash and gypsum. Mangat *et al.* (2006) showed that FGD can be simulated by mixing different combinations of fly ash and gypsum.

1. Experimental

1.1. Materials

The pastes used in this investigation consists of 42.5N Portland cement (C), fly ash (FA), gypsum (G) and water. Table 1 presents the density and the specific surface of cement and FGD materials. Further information regarding the physical and chemical composition of the materials is given elsewhere (Khatib *et al.* 2013a, b). The water/binder was kept constant at 0.5. The binder consists of cement, fly ash and gypsum. Paste P1 represents the reference paste containing 100% C. Mixes P2–P8 contain simulated FGD wastes consisting of different blends of fly ash and gypsum (FA-G blends). The cement was replaced with 25% FA-G blend. The gypsum content in the FA-G blends ranged from 0% (paste P2) to 100% (paste P8).

Table 1. Density and specific surface of materials

	Density (kg/m^3)	Specific surface (m^2/kg)
Cement	3150	376
Fly ash	2180	355
Gypsum	2350	158

Table 2 shows the composition of binder in the various pastes. The basis for the proportions of the simulated FGD is reported elsewhere (Mangat *et al.* 2006; Khatib *et al.* 2008). The paste ID represents the proportions of replacement materials (i.e. fly ash and gypsum). For example, a paste with an ID 75FA25G represents a paste with replacement materials consisting of 75% fly ash and 25% gypsum.

1.2. Mixing

Fly ash and gypsum were mixed by hand until the homogeneity of the FA-G blends was achieved. All

Table 2. Constituents of binder

		Proportions (% weight of binder)		
Paste number	Paste ID	Cement (C)	Gypsum (G)	Fly ash (FA)
P1	REF (100_C)	100	0	0
P2	$100_{FA}0_G$	75	0	25
P3	$95_{FA}5_G$	75	1.25	23.75
P4	$85_{FA}15_G$	75	3.75	21.25
P5	$75_{FA}25_G$	75	6.25	18.75
P6	$50_{FA}50_G$	75	12.5	12.5
P7	$20_{FA}80_G$	75	20	5
P8	$0_{FA}100_G$	75	25	0

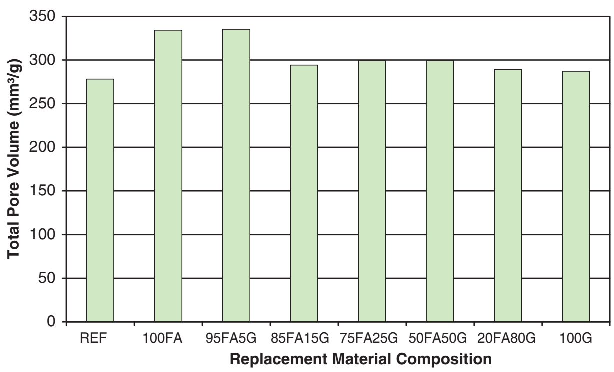

Fig. 1. Influence of FA-G composition on the TPV of pastes

binder constituents were placed in a Hobart mixer and mixed for three minutes until the mixture was homogenous. The water was added over a period of 30 seconds while mixing continued for approximately 5 minutes. The mixing process was interrupted occasionally to remove accumulated material from the paddle and the bottom of the bowl. After five minutes of mixing, the paste was mixed by hand to remove any accumulated material on the paddle and the base of the mixing bowl. The material was regularly remixed during sample preparation to avoid settlement and bleeding.

1.3. Testing

The paste specimens consisted of 50-mm cubes. All pastes were placed in a mist curing room at 20 ± 1 °C and $95 \pm 5\%$ relative humidity for 24 hours. After that, demoulding took place and cubes were crushed for compressive strength and representative samples were taken from the middle of the crushed cube for the determination of porosity and pore size distribution. The sample size used for the analysis was approximately 1 g. The samples were dried in an oven at 70 °C for 48 hours to remove the internal moisture. The samples were then placed in an airtight bottle until testing. Silica gel crystals were added to the bottle to absorb any moisture. The total pore volume (TPV) (i.e. porosity) and pore size distribution were determined using the mercury intrusion porosimetry technique. Further information on the testing technique is found elsewhere (Khatib, Wild 1996; Khatib, Mangat 1999, 2003).

2. Results

Figure 1 shows the TPV of paste containing different FA-G blends at 1 day. The TPV of the FA-G blended pastes (P2–P8) tends to be higher than that exhibited by the reference paste (P1). Pastes P2 and P3 which contain the highest amount of fly ash in the FA-G blend (100% and 95%, respectively) record the highest TPV.

Figures 2–9 show the pore size distribution for pastes P1–P8, respectively, at 1 day of curing (i.e. after demoulding). The shape of the pore distribution curves during the early periods of hydration look similar with and without simulated FGD waste. This is different from the pore size distribution at later ages of hydration (Khatib *et al.* 2012a, b, 2013a, b) where the presence of increasing amounts of simulated FGD shows the emergence of secondary peaks. Figure 10 shows a typical pore size distribution curve at 365 days of curing for

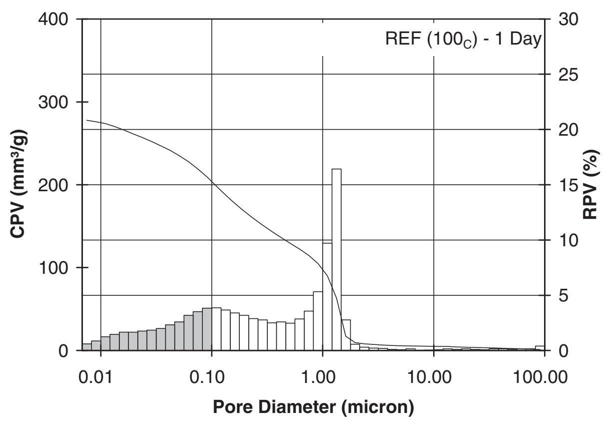

Fig. 2. Pore size distribution of the reference paste P1

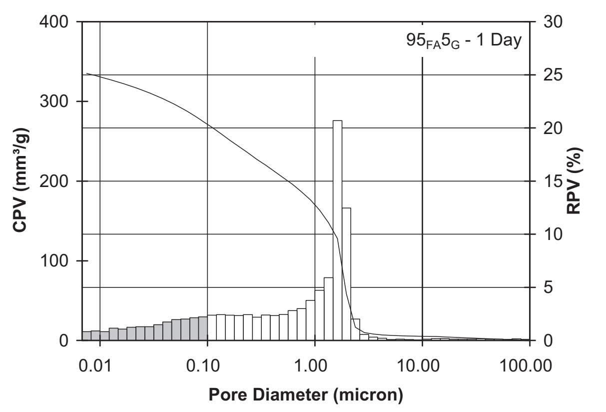

Fig. 4. Pore size distribution of paste P3

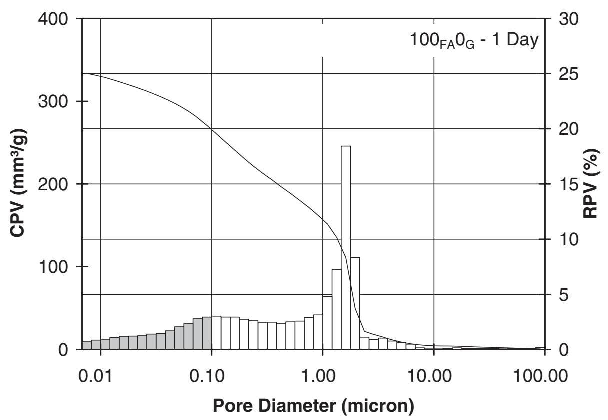

Fig. 3. Pore size distribution of paste P2

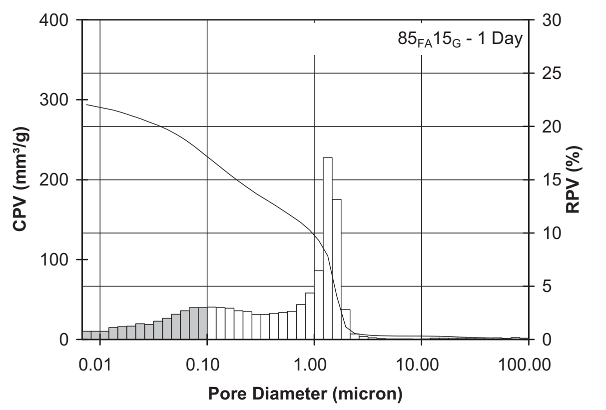

Fig. 5. Pore size distribution of paste P4

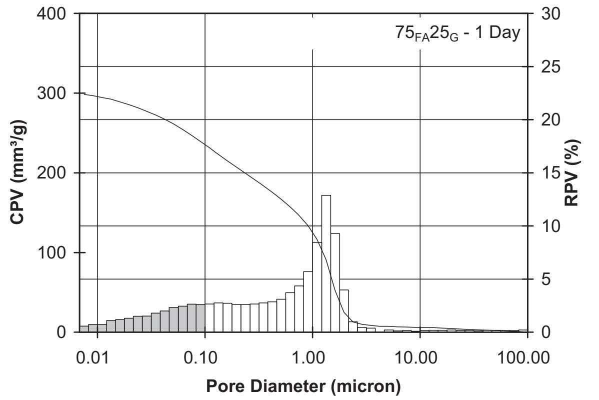

Fig. 6. Pore size distribution of paste P5

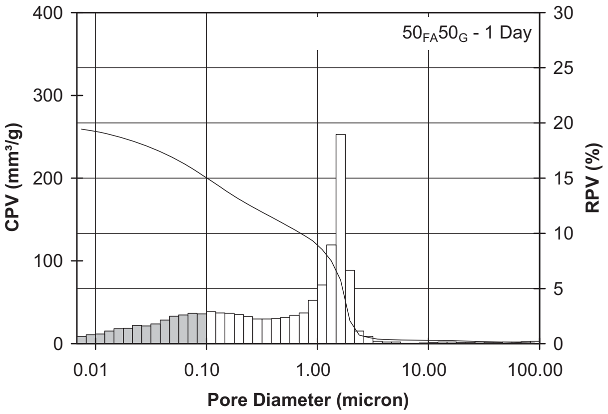

Fig. 7. Pore size distribution of paste P6

FA-G composition of 80–20 (Khatib *et al.* 2012b), where the emergence of a secondary peak is more apparent.

Figure 11 shows the threshold diameter (TD) for mixes containing different FA-G blends. The TD is the diameter before which the pore size distribution curve rises sharply. An increase in the TD tends to indicate a coarser pore structure. The reference mix exhibited a TD of 1.65 µm. Replacing cement with 25% fly ash ($100_{FA}0_G$) increased the TD to more than 2.25 µm. Replacing the fly ash with 5% of gypsum increased the TD. The TD for pastes P4 ($85_{FA}15_G$) and P5 ($75_{FA}25_G$) was lower than the other pastes containing fly ash and gypsum and was similar to the control (P1).

The percentage of small pores (i.e. pores whose diameter is smaller than 0.1 µm) for the various pastes is shown in Figure 12. All pastes with fly ash and gypsum (pastes P2–P8) show a lower percentage of small pores indicating a coarser pore structure in the presence of simulated FGD products. However, gypsum contents replacing more than 5% of the fly ash start showing a higher percentage of small pores compared with paste P3 (95FA5%G) but the trend is not very strong.

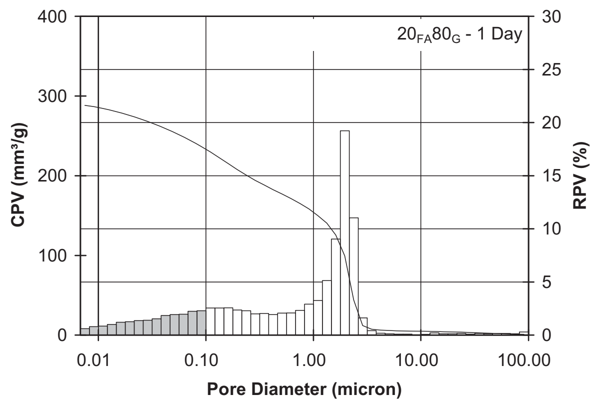

Fig. 8. Pore size distribution of paste P7

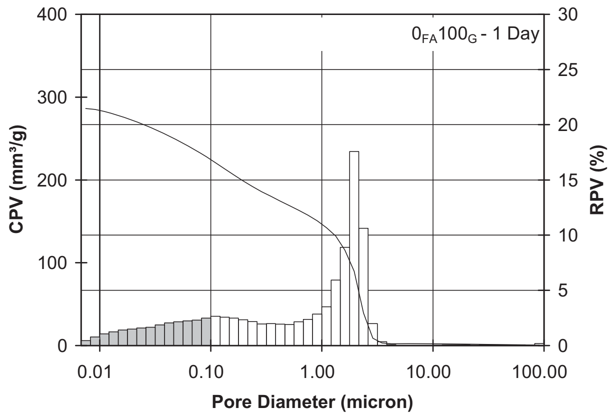

Fig. 9. Pore size distribution of paste P8

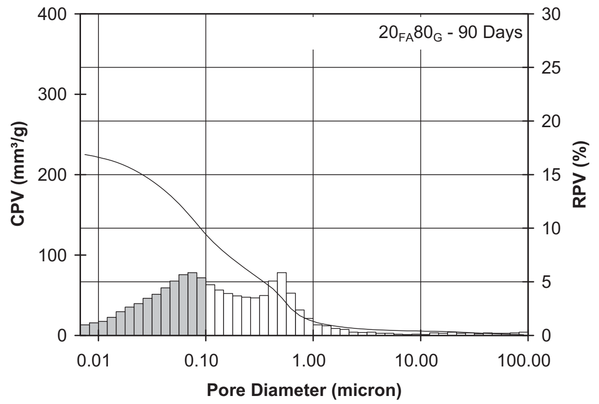

Fig. 10. Pore size distribution of paste P7 at 90 days of curing (Khatib *et al.* 2012b)

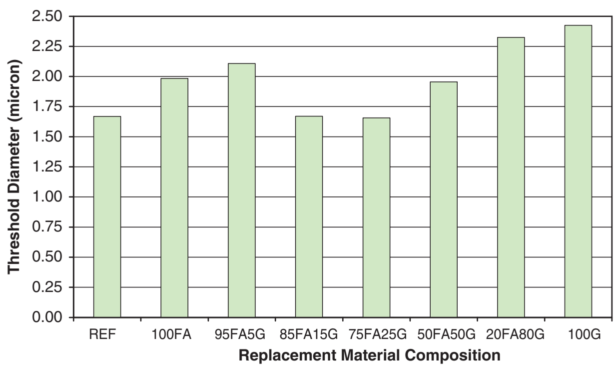

Fig. 11. Influence of simulated FGD on the TD of pastes

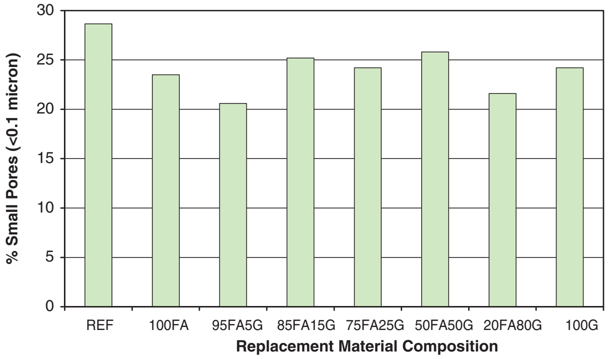

Fig. 12. Influence of simulated FGD on the percentage of small pores (<0.1 m) of pastes

3. Discussion of results

Manmohan and Mehta (1981) reported that replacing cement with fly ash increased pore refinement compared to a reference mix of 100% cement after a certain period of hydration. This was attributed to the pozzolanic properties of the fly ash. The calcium hydroxide (CH) released during cement hydration reacts with the silica and alumina components of the fly ash to form additional hydrated phases. These products fill the open capillary pores, which result in an improvement in the pore structure (Ramezanianpour, Malhotra 1995; Xu, Huang 1992). However, in the present investigation, the pastes were cured only for one day and the production of CH in this period would be very limited for sufficient reaction to take place between the fly ash particles and CH. At 7, 28 and 90 days of curing, the trend is noticeably different (Khatib *et al.* 2012b, 2013a, b).

Using gypsum in cement–fly ash paste enhances the reactivity of fly ash particles (Uchikawa 1986; Wild *et al.* 1995). This was attributed to the formation of sulphate containing C-A-S-H products that form around the fly as particles. However, at 1 day, this was not evident in the present study. Long-term data are reported elsewhere (Khatib *et al.* 2011) which show the effect more clearly. Excessive replacement of fly ash with gypsum can result in a retardation of the hydration process as the increased ettringite formation on the fly ash particles temporarily retards the reaction of fly ash with lime (Wild *et al.* 1995). This does appear to be the case, especially in the mix containing 100% gypsum as replacement blend (i.e. paste P8). The gypsum in the FGD waste produces ettringite in the early ages of hydration coating the fly ash particles and thereby delaying the pozzolanic reaction. In the longer term, the continued ettringite formation fills the pore spaces which may be the reason for the secondary peak on the pore distribution curve. The ettringite provides enhanced sulphate resistance to FGD blended systems (Khatib *et al.* 2008). This makes the FGD materials particularly suitable for sulphate resistance applications.

Conclusions

The following conclusions are based on the results of this investigation:

1) Replacing 25% of cement with different simulated desulphurised waste (FA-G blends) increased the TPV of cement pastes at 1 day of curing. Increasing the gypsum content in the FA-G blend generally increased TPV. Replacing cement with different FA-G blends increased the TD and decreased the percentage of small pores below 0.1 μm (SP), which indicated a decrease in pore refinement compared to the reference paste.
2) Concrete incorporating FGD waste has the potential for use in various applications including masonry blocks and paving slabs. Also, using FGD waste in concrete results in superior sulphate resistance and thereby enhanced durability. This suggests that it can be a suitable material for ground structures.

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